D-21267

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Customer No.: 27182	Confirmation No.: 7022
Serial No.: 10/685,785	Group Art Unit: 1792
Inventors: David M. Thompson et al.	Filed: October 16, 2003
Title: DEPOSITION PROCESSES USING GROUP 8 (VIII) METALLOCENE PRECURSORS	Examiner: E. A. Burkhart

APPEAL BRIEF

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

This is a brief in support of an appeal from the decision of the Examiner dated May 20, 2008. A notice of appeal was filed September 9, 2008 together with a one (1) month extension of time.

REAL PARTY IN INTEREST

In accordance with 37 CFR 41.37(c)(1)(i), Praxair Technology, Inc. is the owner of 100 percent interest in the instant application, which ownership interest is of record in reel No. 014303, frame No. 0142, recorded February 3, 2004.

RELATED APPEALS AND INTERFERENCES

In accordance with 37 CFR 41.37(c)(1)(ii), no other appeals or interferences are known to Appellants, Appellants' legal representative or assignee which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

STATUS OF CLAIMS

In accordance with 37 CFR 41.37(c)(1)(iii), the status of all claims is as follows: the rejected claims include claims 1-22, 24, 25, 28-32 and 34-39, the canceled claims include claims 26, 27 and 33, the withdrawn claims include claim 23, and the appealed claims include all of the rejected claims, i.e., 1-22, 24, 25, 28-32 and 34-39.

STATUS OF AMENDMENTS

In accordance with 37 CFR 41.37(c)(1)(iv), no amendment was filed subsequent to final rejection.

SUMMARY OF CLAIMED SUBJECT MATTER

In accordance with 37 CFR 41.37(c)(1)(v), the following is a concise explanation of the subject matter defined in each of the independent claims involved in this appeal, i.e., independent claims 1 and 2.

Independent claim 1 relates to a process for producing a film, coating or powder by decomposing at least one asymmetric metallocene precursor having a general formula CpMCp', where M is a metal selected from Ru, Os and Fe; Cp is a first substituted cyclopentadienyl or a cyclopentadienyl-like moiety; and Cp' is a second substituted cyclopentadienyl or a cyclopentadienyl-like moiety different from Cp; thereby producing the film, coating or powder. The decomposition is conducted in the presence of a solvent fluid. See, for example, page 4, line 1 through page 6, line 5, and original claim 33 of Appellants' specification.

Independent claim 2 relates to a process for producing a film by decomposing at least one precursor in the presence of a substrate, thereby forming a film on the substrate. The decomposition is thermal, chemical, photochemical or plasma-activated. The precursor has a general formula CpMCp', where M is a metal selected from Ru, Os and Fe; Cp is a first substituted cyclopentadienyl or indenyl moiety; and Cp' is a second substituted cyclopentadienyl or indenyl moiety different from Cp. The decomposition is conducted in the presence of a solvent fluid. The film includes ruthenium, osmium or iron metal, or ruthenium oxide, osmium oxide or iron oxide. See, for example, page 4, line 1 through page 6, line 5, and original claim 33 of Appellants' specification.

GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

In accordance with 37 CFR 41.37(c)(1)(vi), the grounds of rejection presented for review on appeal are as follows:

whether claims 1-13, 16-22, 24, 25, 28-32, 34 and 37-39 should be rejected under 35 U.S.C. 103(a) as being unpatentable over Okamoto ('669) in view of Sievers et al. ('093); and

whether claims 14, 15, 35 and 36 should be rejected under 35 U.S.C. 103(a) as being unpatentable over Okamoto ('669) in view of Sievers et al. ('093) and further in view of Soininen et al. ('740).

ARGUMENT

In accordance with 37 CFR 41.37(c)(1)(vii), the contentions of Appellants with respect to the above grounds for rejection presented for review are set forth below.

REJECTION UNDER 35 U.S.C. 103(a)

The ground for rejection presented for review here is whether claims 1-13, 16-22, 24, 25, 28-32, 34 and 37-39 should be rejected under 35 U.S.C. 103(a) as being unpatentable over Okamoto ('669) in view of Sievers et al. ('093). Claims 19 and 20 are also argued separately below.

The primary reference, Okamoto, discloses metal-organic vapor-phase epitaxy using an organic ruthenium compound having two 5-membered rings. The two 5-membered rings can be substituted with at least one alkyl group selected from CH_2CH_3, $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$, $C(CH_3)_3$, $CH_2(C_6H_5)$, $COCH_3$, $COOCH_3$, and CH_2OCH_3. Note that CH_3 is excluded as a permissible alkyl group. Okamoto does not disclose, suggest or exemplify Appellants' claimed process for decomposing an asymmetric metallocene precursor.

This substitution pattern of ruthenium compounds is exemplified by Okamoto in several embodiments. See, for example, column 4, line 61 through column 7, line 57. The organic ruthenium embodiments are as follows:

Embodiment 1 – bis(ethylcyclopentadiene)ruthenium. This compound is symmetric. The two cyclopentadienyl groups are both substituted with ethyl.

Embodiment 2 – bis(benzyl)(cyclopentadienyl)ruthenium. This compound is symmetric. The two cyclopentadienyl groups are both substituted with benzyl.

Embodiment 3 – bis(t-butylcyclopentadiene)ruthenium. This compound is symmetric. The two cyclopentadienyl groups are both substituted with t-butyl.

Embodiment 4 – bis(propylcyclopentadiene)ruthenium. This compound is symmetric. The two cyclopentadienyl groups are both substituted with propyl.

Embodiment 5 – acetylruthenocene. This compound is asymmetric, however, only one cyclopentadienyl group is substituted with acetyl. The other cyclopentadienyl group is unsubstituted.

Embodiment 5 (comparative) – bis(cyclopentadienyl)ruthenium. This compound is symmetric, however, the two cyclopentadienyl groups are both unsubstituted.

Embodiment 5 (comparative) – bis(pentamethylcyclopentadienyl)ruthenium. This compound is symmetric. The two cyclopentadienyl groups are both fully substituted with methyl.

Embodiment 5 (comparative) – bis(methylcyclopentadiene)ruthenium. This compound is symmetric. The two cyclopentadienyl groups are both substituted with methyl.

As can be seen from the above embodiments of Okamoto, nowhere does Okamoto even remotely disclose, suggest or exemplify asymmetric metallocene precursors used in deposition processes as claimed by Appellants and the unexpected advantages resulting therefrom. Okamoto actually teaches away from Appellants' claimed invention by disclosing and exemplifying only symmetric compounds or compounds in which only one 5-membered ring is substituted.

Clearly, it is only by hindsight that the Examiner could impute to the compounds disclosed and exemplified by Okamoto an asymmetric substitution pattern involving two substituted cyclopentadienyl or cyclopentadienyl-like rings to arrive at the instantly claimed process for decomposing asymmetric metallocene compounds, and such hindsight obviousness after the invention has been made is not the proper test. See In re Carroll 601 F2d 1184, 202 USPQ 571.

The secondary reference, Sievers et al., adds nothing to make up for the deficiencies of Okamoto. Seivers et al. discloses a method for depositing a film of a desired material on a substrate by dissolving at least one reagent in a supercritical fluid comprising at least one solvent. Sievers et al. is even more remotely removed from Appellants' claimed invention than Okamoto. Nowhere does Sievers et al. even remotely disclose, suggest or exemplify asymmetric metallocene precursors used in deposition processes as claimed by Appellants and the unexpected advantages resulting therefrom.

From Example 10 of Appellants' specification, properties of films deposited using 1-methyl,1'-ethylruthenocene were measured and were compared with those of films produced using 1,1'-diethylruthenocene. Films were deposited on a 3-inch wafer using an apparatus such as described in the examples. The wafer temperature was 330°C, the precursor vaporization temperature was 70-90°C, the chamber pressure was 2 Torr, the oxygen flow rate was 200 sccm, the nitrogen flow rate was 550 sccm, the deposition time was 5 minutes, and the film growth rate was 10-60 nm/minute. Sheet resistance was measured with four-point probe, perpendicular to major flat and 5 mm intervals (major flat=0 mm). The results are shown in Figs. 14, 15 and 16 of Appellants' specification.

Fig. 14 describes the measured sheet resistance of films deposited from $(EtCp)_2Ru$ and (EtCp)(MeCp)Ru, as a function of vaporizer temperature. Vaporizer temperature was varied, while all other experimental conditions (temperature, pressure, etc.) were fixed. The data was measured at the center of the substrate. This figure shows that the films deposited using (EtCp)(MeCp)Ru exhibited lower sheet resistance, compared to the films deposited from $(EtCp)_2Ru$. This can be attributed to the higher concentration of (EtCp)(MeCp)Ru in the process gas, compared to $(EtCp)_2Ru$, at the same vaporizer temperature. This difference in precursor concentration is believed to result from the difference in vapor pressure.

The wafer was cleaved and the film thickness, measured by cross-sectional SEM, is shown in Fig. 15. Under identical conditions, over the same period of time, films produced from 1-methyl,1'-ethylruthenocene were thicker than the films formed employing 1,1'-diethylruthenocene. This result also was attributed to the higher vapor pressure of 1-methyl,1'-ethylruthenocene.

The resistivity of these films, shown in Fig. 16, was calculated using the measured values of sheet resistance and thickness. X-ray diffraction data also was obtained and indicated that crystallites observed in SEM data were composed of Ru. In addition, X-ray photoelectron spectroscopy data was gathered as a function of depth of the film. The data indicated that oxygen was present near the surface of the films and that the amount of oxygen present in the film decreased, as one goes deeper into the film. It appeared that less oxygen was present at depth in films produced using 1-methyl,1'-ethylruthenocene than in films formed from 1,1'diethylruthenocene.

The compounds decomposed in the processes of this invention provide additional options and flexibility to existing methods for producing Ru-, Os-, or Febased thin films by CVD. Some of these compounds, for example, are liquid at room temperature and have higher vapor pressure than conventional precursors. It has been found, for instance, that 1-methyl,1'-ethylruthenocene has a higher vapor pressure than 1,1'-diethylruthenocene. Higher vapor pressure presents economic advantages such as increased productivity and lower film manufacturing costs. Functionalization of the cyclopentadienyl rings in the compounds of the invention is believed to modify properties such as solubility, vapor pressure, decomposition, combustion and other reaction pathways, reduction/oxidation potentials, geometry, preferred orientations and electron density distribution through modification of the cyclopentadienyl rings. Thus a specific precursor can be selected for a desired application. Except for hydrogen and carbon, many of the precursors described by Appellants, such as, for instance, alkyl-substituted metallocenes, do not include extraneous atoms and thus materials formed by their decomposition generally are free from impurities. In some other cases, the presence of oxygen atoms in the organic substituent groups may favor the formation of metal oxide films, coatings or powders.

Rejection of Claims 19-20 under 35 U.S.C. 103(a)

Appellants separately argue the patentability of claims 19 and 20 grouped in the above rejection. In view of the comparative data from Example 10 of Appellants' specification showing the unexpectedly improved properties of films deposited using 1-methyl, 1'-ethylruthenocene compared with films produced using 1,1'-ethylruthenocene, it is submitted that claims 19 and 20 are clearly patentable over the cited references. The comparative data from Example 10 of Appellants' specification is detailed above. For these reasons and also for the reasons set forth above in response to the above rejection, Appellants submit that the rejection of claims 19 and 20 under 35 U.S.C. 103(a) is improper and should be reversed.

For the reasons set forth above, Appellants submit that the above rejection of claims 1-13, 16-22, 24, 25, 28-32, 34 and 37-39 under 35 U.S.C. 103(a) is improper and should be reversed.

REJECTION UNDER 35 U.S.C. 103(a)

The ground for rejection presented for review here is whether claims 14, 15, 35 and 36 should be rejected under 35 U.S.C. 103(a) as being unpatentable over Okamoto ('669) in view of Sievers et al. ('093) and further in view of Soininen et al. ('740).

The primary reference, Okamoto, and the secondary reference, Sievers et al., have been discussed above. The other secondary reference, Soininen et al., adds nothing to make up for the deficiencies of Okamoto and Sievers et al. Soininen et al. discloses a method for depositing a metal oxide thin film on a substrate surface and thereafter reducing the metal oxide thin film into a metallic form with an organic reducing agent. As with Sievers et al., Soininen et al. likewise is even more remotely removed from Appellants' claimed invention than Okamoto. Nowhere does Soininen et al. even remotely disclose, suggest or exemplify asymmetric metallocene precursors used in deposition processes as claimed by Appellants and the unexpected advantages resulting therefrom.

For these reasons and also for the reasons set forth above in response to the other rejection, Appellants submit that the above rejection of claims 14, 15, 35 and 36 under 35 U.S.C. 103(a) is improper and should be reversed.

CLAIMS APPENDIX

In accordance with 37 CFR 41.37(c)(1)(viii), the attached Claims Appendix contains a copy of all claims involved in this Appeal.

EVIDENCE APPENDIX

In accordance with 37 CFR 41.37(c)(1)(ix), the attached Evidence Appendix contains a copy of all evidence entered by the Examiner and relied upon by Appellants in this Appeal.

RELATED PROCEEDINGS APPENDIX

In accordance with 37 CFR 41.37(c)(1)(x), the attached Related Proceedings Appendix contains a copy of all decisions rendered by a court or the board involving this Appeal.

This brief in support of an appeal is due November 9, 2008. Submitted herewith is the required fee for filing a brief in support of an appeal. Please charge fees/surcharge which may be required by this paper, or credit any overpayment, to Deposit Account No. 16-2440.

Respectfully submitted,

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November 7, 2008
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CLAIMS APPENDIX

Claims on Appeal

1. A process for producing at least one member of the group consisting of a film, a coating and a powder, comprising the step of decomposing at least one asymmetric metallocene precursor having a general formula CpMCp',

where

M is a metal selected from the group consisting of Ru, Os and Fe;

Cp is a first substituted cyclopentadienyl or a cyclopentadienyl-like moiety that includes at least one substituent group D_1;
Cp' is a second substituted cyclopentadienyl or a cyclopentadienyl-like moiety that includes at least one substituent group D_1';
wherein
D_1 is different from D_1';
D_1 is selected from the group consisting of:

X;
$C_{a1}H_{b1}X_{c1}$;
$C_{a2}H_{b2}X_{c2}(C{=}O)C_{a1}H_{b1}X_{c1}$;
$C_{a2}H_{b2}X_{c2}OC_{a1}H_{b1}X_{c1}$;
$C_{a2}H_{b2}X_{c2}(C{=}O)OC_{a1}H_{b1}X_{c1}$; and
$C_{a2}H_{b2}X_{c2}O(C{=}O)C_{a1}H_{b1}X_{c1}$;

where

X is a halogen atom;
a1 is an integer from 2 to 8;
b1 is an integer from 0 to 2(a1)+1 – c1;
c1 is an integer from 0 to 2(a1)+1 – b1;

b1 + c1 is at least 1;

a2 is an integer from 0 to 8;

b2 is an integer from 0 to 2(a2) + 1 – c2;

c2 is an integer from 0 to 2(a2) + 1 – b2; and

D1' is selected from the group consisting of:

X

$C_{a1}H_{b1}X_{c1}$,

$C_{a2}H_{b2}X_{c2}(C{=}O)C_{a1}H_{b1}X_{c1}$,

$C_{a2}H_{b2}X_{c2}OC_{a1}H_{b1}X_{c1}$,

$C_{a2}H_{b2}X_{c2}(C{=}O)OC_{a1}H_{b1}X_{c1}$, and

$C_{a2}H_{b2}X_{c2}O(C{=}O)C_{a1}H_{b1}X_{c1}$

where,

X is Fl, Cl, Br or I;

a1 is an integer from 1 to 8;

b1 is an integer from 0 to 2(a1)+1 – c1;

c1 is an integer from 0 to 2(a1)+1 – b1;

b1 + c1 is equal to or greater than 1;

a2 is an integer from 0 to 8;

b2 is an integer from 0 to 2(a2)+1 – c2;

c2 is an integer from 0 to 2(a2)+1 – b2; and

b2 + c2 is equal to or greater than 1,

thereby producing the film, coating or powder; wherein the decomposition is conducted in the presence of a solvent fluid.

2. A process for producing a film, comprising the step of decomposing at least one precursor in the presence of a substrate, wherein the decomposition is thermal, chemical, photochemical or plasma-activated, and said precursor has a general formula CpMCp',

where

M is a metal selected from the group consisting of Ru, Os and Fe;

Cp is a first substituted cyclopentadienyl or indenyl moiety that includes at least one substituent group D_1;

Cp' is a second substituted cyclopentadienyl or indenyl moiety that includes at least one substituent group D_1';

wherein

D_1 is different from D_1';

D_1 is selected from the group consisting of:

  X;

  $C_{a1}H_{b1}X_{c1}$;

  $C_{a2}H_{b2}X_{c2}(C{=}O)C_{a1}H_{b1}X_{c1}$;

  $C_{a2}H_{b2}X_{c2}OC_{a1}H_{b1}X_{c1}$;

  $C_{a2}H_{b2}X_{c2}(C{=}O)OC_{a1}H_{b1}X_{c1}$; and

  $C_{a2}H_{b2}X_{c2}O(C{=}O)C_{a1}H_{b1}X_{c1}$;

where

  X is a halogen atom;

  a1 is an integer from 2 to 8;

  b1 is an integer from 0 to 2(a1)+1 – c1;

  c1 is an integer from 0 to2(a1)+1 – b1;

  b1 + c1 is at least 1;

  a2 is an integer from 0 to 8;

  b2 is an integer from 0 to 2(a2) + 1 – c2;

  c2 is an integer from 0 to 2(a2) + 1 – b2; and

D1' is selected from the group consisting of:

  X

  $C_{a1}H_{b1}X_{c1}$,

  $C_{a2}H_{b2}X_{c2}(C{=}O)C_{a1}H_{b1}X_{c1}$,

  $C_{a2}H_{b2}X_{c2}OC_{a1}H_{b1}X_{c1}$,

  $C_{a2}H_{b2}X_{c2}(C{=}O)OC_{a1}H_{b1}X_{c1}$, and

$C_{a2}H_{b2}X_{c2}O(C{=}O)C_{a1}H_{b1}X_{c1}$

where,

X is Fl, Cl, Br or I;

a1 is an integer from 1 to 8;

b1 is an integer from 0 to 2(a1)+1 – c1;

c1 is an integer from 0 to 2(a1)+1 – b1;

b1 + c1 is equal to or greater than 1;

a2 is an integer from 0 to 8;

b2 is an integer from 0 to 2(a2)+1 – c2;

c2 is an integer from 0 to 2(a2)+1 – b2; and

b2 + c2 is equal to or greater than 1,

thereby forming a film on the substrate; wherein the decomposition is conducted in the presence of a solvent fluid; and wherein the film includes ruthenium, osmium or iron metal, or ruthenium oxide, osmium oxide or iron oxide.

3. The process of Claim 2, wherein either or both of Cp and Cp' moiety includes at least one additional substituent, D_x, selected from the group consisting of:

X

$C_{a1}H_{b1}X_{c1}$,

$C_{a2}H_{b2}X_{c2}(C{=}O)C_{a1}H_{b1}X_{c1}$,

$C_{a2}H_{b2}X_{c2}OC_{a1}H_{b1}X_{c1}$,

$C_{a2}H_{b2}X_{c2}(C{=}O)OC_{a1}H_{b1}X_{c1}$, and

$C_{a2}H_{b2}X_{c2}O(C{=}O)C_{a1}H_{b1}X_{c1}$,

where,

X is Fl, Cl, Br or I;

a1 is an integer from 0 to 8;

b1 is an integer from 0 to 2(a1)+1 – c1;

c1 is an integer from 0 to 2(a1)+1 – b1;

b1 + c1 is equal to or greater than 1;

a2 is an integer from 0 to 8;
b2 is an integer from 0 to2(a2)+1 – c2;
c2 is an integer from 0 to 2(a2)+1 – b2; and
b2 + c2 is equal to or greater than 1.

4. The process of Claim 2, wherein said precursor is vaporized and the vapor is directed into a deposition reactor housing the substrate.

5. The process of Claim 4, wherein the deposition reactor is at a pressure in the range of from about 0.01 Torr and about 760 Torr.

6. The process of Claim 5, wherein the deposition reactor is at a pressure in the range of from about 0.1 Torr and about 760 Torr.

7 The process of Claim 6, wherein the deposition reactor is at a pressure in the range of from about 1 Torr and about 50 Torr.

8. The process of Claim 2, wherein the substrate is at a temperature in the range of from about 75°C to about 700°C.

9. The process of Claim 8, wherein the substrate is at a temperature in the range of from about 250°C to about 450°C.

10. The process of Claim 2, wherein the substrate is comprised of a material selected from the group consisting of a metal; a metal silicide; a semiconductor; an insulator and a barrier material.

11. The process of Claim 2, wherein the substrate is a patterned wafer.

12. The process of Claim 2, wherein the process includes decomposing at least one additional organometallic precursor.

13. The process of Claim 2, wherein vapor of said precursor is combined with a carrier gas.

14. The process of Claim 2, wherein vapor of said precursor is combined with an oxidizing component.

15. The process of Claim 14 wherein the oxidizing component is selected from the group consisting of oxygen, ozone and nitrous oxide.

16. The process of Claim 2, wherein vapor of said precursor is combined with at least one other gas or vapor component to form a process gas.

17. The process of Claim 16, wherein the process gas is supplied to a deposition reactor.

18. The process of Claim 17 wherein an exhaust gas is exhausted from the deposition reactor.

19. The process of Claim 2, wherein said precursor is 1-methyl,1'-ethyl ruthenocene.

20. The process of Claim 2 wherein D_1 is methyl and D_1' is selected from the group consisting of ethyl, propyl, isopropyl, n-butyl, sec-butyl and tert-butyl.

21. The process of Claim 2, wherein D_1 is ethyl and D_1' is selected from the group consisting of propyl, isopropyl, n-butyl, sec-butyl and tert-butyl.

22. The process of Claim 2, wherein D_1 is propyl and D_1' is selected from the group consisting of isopropyl, n-butyl, sec-butyl and tert-butyl.

23. (withdrawn)

24. The process of Claim 2, wherein D_1 is n-butyl and D_1' is selected from the group consisting of sec-butyl and tert-butyl.

25. The process of Claim 2, wherein D_1 is sec-butyl and D_1' is tert-butyl.

26. (canceled)

27. (canceled)

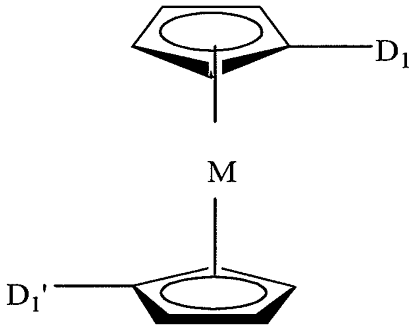
28. The process of Claim 2, wherein the film has a thickness that is less than about 500 nanometer.

29. The process of Claim 2, wherein the film has a thickness that is less than about 200 nanometer.

30. The process of Claim 2, wherein the film has a thickness that is less than 50 nanometer.

31. The process of Claim 2, wherein the film has a thickness that is less than about 30 nanometer.

32. The process of Claim 2, wherein said precursor is represented by the following molecular formula:



33. (canceled)

34. The process of Claim 33, wherein the solvent fluid is a near critical or supercritical fluid.

35. The process of Claim 2, wherein film is deposited on the substrate in layers.

36. The process of Claim 35, wherein the film is deposited by sequential chemical vapor deposition, atomic layer nucleation or atomic layer deposition.

37. The process of Claim 1, wherein the film, coating or powder is produced by a gas phase deposition.

38. The process of Claim 1, wherein the film, coating or powder is produced *in-situ.*

39. The process of Claim 2, wherein D_1 is isopropyl and D_1' is selected from the group consisting of n-butyl, sec-butyl and tert-butyl.

EVIDENCE APPENDIX

None.

RELATED PROCEEDIGS APPENDIX

None.